

Bound magnetic polarons in the very dilute regime

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We study bound magnetic polarons (BMP) in a very diluted magnetic semiconductor $\text{Cd}_{1-x}\text{Mn}_x\text{Te}$ ($x < 0.01$) by means of site selective spectroscopy. In zero magnetic field we detect a broad and asymmetric band with a characteristic spectral width of about 5 meV. When external magnetic fields are applied a new line appears in the emission spectrum. Remarkably, the spectral width of this line is reduced greatly down to 240 μeV . We attribute such unusual behavior to the formation of BMP, effected by sizable fluctuations of local magnetic moments. The modifications of the optical spectra have been simulated by the Monte-Carlo method and calculated within an approach considering the nearest Mn ion. A quantitative agreement with the experiment is achieved without use of fitting parameters. It is demonstrated that the low-energy part of the emission spectra originates from the energetic relaxation of a complex consisting of a hole and its nearest Mn ion. It is also shown that the contribution to the narrow line arises from the remote Mn ions.

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I. INTRODUCTION

An intriguing phenomenon in diluted magnetic semiconductors (DMS) is the formation of bound magnetic polarons^{1,2}. The bound magnetic polaron (BMP) is a local ordering of magnetic moments induced by the exchange interaction with a localized carrier. Most BMP studies, both experimental and theoretical, have been performed so far in a regime of the mean-field approach (when $N_{\text{Mn}}a_B^3 \gg 1$)^{3,4,5,6,7,8}. Here, $N_{\text{Mn}} = xN_0$ is the concentration of magnetic ions, N_0 is the concentration of cations, and a_B is the localization radius. This approach implies that the localized carrier interacts with a infinite number of Mn^{2+} ions, and hence it is typically applicable for high and moderate manganese concentrations ($x > 0.01$). At present systems with a countable number of magnetic moments attract growing interest⁹. This corresponds to the very dilute regime $N_{\text{Mn}}a_B^3 \ll 1$, i.e. when on average one carrier interacts with one (or few) Mn ion(s). Clearly, at this condition the mean-field approach is not an appropriate model.

Up to now bound magnetic polarons have not been observed in a very dilute regime. This is because their observation requires the polaron formation time τ_F to be shorter than the life time τ of nonequilibrium carriers, $\tau_F < \tau$. In DMS with $x \gtrsim 0.1$ this condition is fulfilled. However, in samples with lower Mn concentrations $x \leq 0.01$ the polaron formation time is of the order $\tau_F \sim 10^{-4} \div 10^{-6} \text{ s}$ ^{10,11}. Therefore, the BMP formation process is interrupted by exciton recombination (with characteristic time $\tau \sim 10^{-9} \text{ s}$)¹².

In this paper we study BMP in bulk $\text{Cd}_{1-x}\text{Mn}_x\text{Te}$ samples with very low Mn concentration ($x < 0.01$), i.e. at the condition $N_{\text{Mn}}a_B^3 \ll 1$. In order to avoid the above problem of BMP detection in the very dilute regime we use resonant (selective) excitation of donor-acceptor (DA) pairs with transition energies⁴

$$E_{\text{DA}} = E_g - E_D - E_A - e^2/\epsilon\rho. \quad (1)$$

Here, E_D and E_A are the binding energies of donors and acceptors respectively, E_g is the band gap and ϵ is the dielectric constant in $\text{Cd}_{1-x}\text{Mn}_x\text{Te}$. As follows from Eq. (1) by changing the excitation energy $E_{\text{ex}} = E_{\text{DA}}$ one can selectively excite pairs with a given DA separation ρ . Because of the weak overlap [$\sim \exp(-\rho/a_B)$] of the donor and acceptor wavefunctions, the pairs with large ρ are characterized by a long recombination time $\tau > \tau_F$. As a result the bound magnetic polaron forms before the recombination occurs. Without polaronic effects such resonantly excited pairs should manifest themselves in emission spectra as a narrow line of width within either the inverse recombination time (\hbar/τ) or the laser line width.

II. EXPERIMENT

The bulk $\text{Cd}_{1-x}\text{Mn}_x\text{Te}$ samples with Mn concentrations $x = 0.003, 0.005, 0.02$ have been grown by the Bridgman technique. The crystals are nominally undoped. The concentration of residual impurities (both donors and acceptors) is about 10^{16} cm^{-3} , which is much lower than the Mn concentration N_{Mn} . As grown crystals are usually p-type due to excess of Te or Cd-vacancies. Note, for acceptors with the Bohr radius $a_B = 10 \text{ \AA}$ and $x = 0.005$ ($N_{\text{Mn}} = 7 \times 10^{19} \text{ cm}^{-3}$) the relationship is $N_{\text{Mn}}a_B^3 = 0.07$. In the experiments we used $4 \times 4 \times 0.3 \text{ mm}$ pieces cleaved out along the (110) plane from the massive monocrystals. All measurements were carried out at a temperature $T = 1.6 \text{ K}$. External magnetic fields were applied either perpendicular to the sample plane (Faraday geometry) or in the sample plane (Voigt geometry). The photoluminescence (PL) was excited by a He-Ne laser or a tunable Ti-sapphire laser pumped by an Ar-ion laser. The excitation density was about 5 W/cm^2 . The laser beam was directed onto the samples at the angle close to the normal (axis [110]), and the emission was registered in the backscattering geometry. A polarizer (in

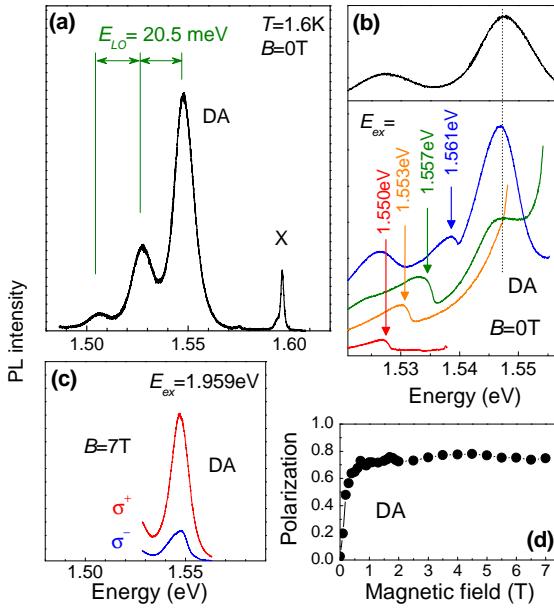


FIG. 1: (Color online) (a) Zero-field PL spectrum of the $\text{Cd}_{0.995}\text{Mn}_{0.005}\text{Te}$ sample excited by a He-Ne laser ($E_{ex} = 1.959$ eV). (b) PL spectra under quasiresonant excitation, the excitation energies (E_{ex}) being shown in the panel. Arrows indicate emission bands which are related to the BMP formation. PL in the same spectral range but under nonresonant excitation [as in (a)] is given in the upper part for comparison. (c) PL spectra of DA pairs recorded in σ^+ and σ^- circular polarizations in an external magnetic field $B = 7$ T applied in Faraday geometry. The excitation conditions are the same as in (a). (c) Degree of circular polarization vs magnetic field detected at the DA band.

combination with a quater-wave plate) was (were) used to linearly (circularly) polarize the excitation. The degree of PL polarization was detected with use of a photo-elastic modulator and a two-channel photon counter.

We found qualitatively very similar behavior in all samples studied. In the following we present experimental results for one piece cleaved out from the bulk $\text{Cd}_{0.995}\text{Mn}_{0.005}\text{Te}$ sample. Figure 1(a) shows the PL spectrum excited above the CdTe band gap E_g (He-Ne laser with $E_{ex} = 1.959$ eV). The high-energy line (X) is attributed to the bound exciton. At low-energy part of the PL spectrum we observe a broad band associated with recombination of DA pairs and its phonon replicas. These replicas are separated by 20.5 meV, which corresponds to the LO-phonon energy in CdTe¹³. Application of external magnetic fields in Faraday geometry results in the circularly polarized emission already in low fields [Fig. 1(c)]. Such a behavior is typical for magnetic semiconductors. Figure 1(d) demonstrates the degree of circular polarization vs magnetic field detected at the DA band. It saturates rapidly on a 75% level.

In order to study bound magnetic polarons we use the site selective spectroscopy¹⁴. We resonantly excite DA pairs and record BMP spectra shifted towards lower energies with respect to the excitation energy E_{ex} (the Stokes

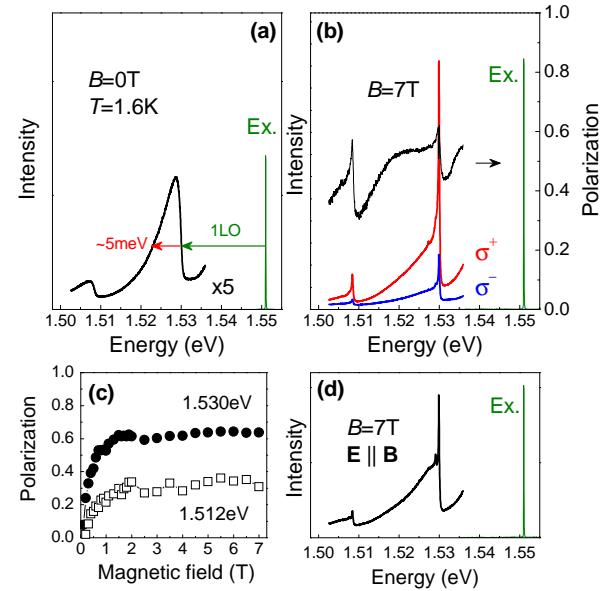


FIG. 2: (Color online) (a) BMP spectrum obtained under resonant excitation (Ex.) to the DA band ($E_{ex} = 1.551$ eV) in zero magnetic field. (b) BMP and BMP-polarization spectra obtained under the same excitation conditions as in (a) but in magnetic field $B = 7$ T applied in Faraday geometry. (c) degree of circular polarization vs magnetic field detected at different energies. (d) BMP spectrum obtained in Voigt geometry when the polarization axis of the excitation (E) is parallel to the field direction ($E \parallel B$).

shift). A set of PL spectra for different E_{ex} is presented in Fig. 1(b). A new emission band (indicated by arrows), being observed on the top of the DA photoluminescence, clearly follows the laser line which is a fingerprint of the BMP formation. The most pronounced results have been obtained for $E_{ex} = 1.551$ eV, as also shown in Fig. 2. In order to avoid scattered light from the laser we detect such BMP spectra at the first phonon replica.

In zero magnetic field the BMP spectrum represents itself as an asymmetric band with the 5-meV-tail towards low energies [Fig. 2(a)]. Our estimations (given below) show that this value is in agreement with the BMP energy as well as with its root-mean-square fluctuations. Such a behavior is an essential deviation from the case of high Mn concentrations ($N_{\text{Mn}}a_B^3 \gg 1$), where the Stokes shift is larger than the line width, giving rise to a distinct emission line shifted from the excitation by the BMP energy¹⁴.

The most drastic changes, however, occur in external magnetic fields applied in Faraday geometry [Fig. 3(a)]. A new line appears at the resonant energy (i.e., there is no Stokes shift at all)¹⁵. With growing magnetic field the amplitude of this line increases and the width reduces greatly. In strong enough magnetic fields ($B > 3$ T) the width saturates on a 240-μeV-level [see also Fig. 2(b)]. The circular polarization of this line is about 65%, and its dependence on the magnetic field [Fig. 2(c)] follows

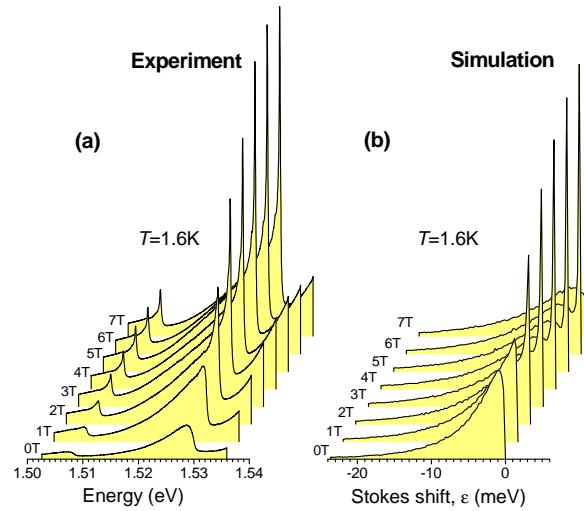


FIG. 3: (Color online) Evolution of BMP spectra with growing magnetic field: (a) experiment and (b) the Monte-Carlo simulation. Note, in (b) no fitting parameters are used. The PL spectra are shifted for clarity.

that for the DA emission under nonresonant excitation [Fig. 1(d)]. One more lineament of this new line: Its intensity reduces under excitation by the light being linearly polarized along the magnetic field direction applied in Voigt geometry [see Fig. 2(d)]. However, a deviation of the field direction from the sample plane or the polarization axis from the field direction restores the amplitude of this line.

As we show in Sec. III, the evolution of PL spectra presented in Fig. 3(a) cannot be described in terms of the mean-field theory, and hence this requires an alternative approach. First, we discuss the asymmetric band observed in zero magnetic field. Resonant excitation generates DA pairs with a certain energy $E_{DA} = E_{ex}$ depending on donor-acceptor separation ρ [pairs (i) and (iii) in Fig. 4(a)]. DA pairs with transition energies different from the excitation energy $E_{DA} \neq E_{exc}$ are not excited [pair (ii) in Fig. 4(a)]. The observation of the asymmetric band in Fig. 2(a) we attribute to the BMP formation accompanied by relaxation to the ground state. The dominant contribution to the polaron shift arises from the hole. This is because the absolute value of the $p-d$ exchange constant is larger than the absolute value of the $s-d$ exchange, and the Bohr radius of the acceptor is smaller than that of the donor^{1,2}. In this approach the line width is explained by the dispersion of the polaron shifts induced by static fluctuations of Mn concentration. For instance, pair (iii) in Fig. 4(a) shows a larger polaron shift than pair (i). Because on average less than one Mn falls into the volume restricted by the acceptor Bohr radius, the root-mean-square fluctuations appear to be comparable with the polaron shift. Its value can be estimated from the line width in Fig. 2(a), $\Gamma \approx 5$ meV.

Strong enough magnetic fields suppress the polaron formation¹⁶, and one would expect the disappearance of

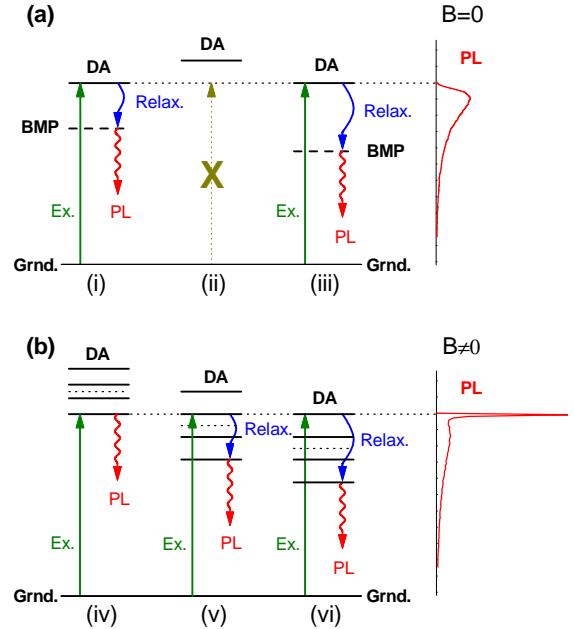


FIG. 4: (Color online) Formation of BMP spectra under selective excitation (Ex.) in (a) zero and (b) strong magnetic fields. The roman numerals in brackets enumerate different DA pairs.

the low-energy tail. However, our experiments show the opposite behavior: This tail preserves and a new narrow intense line appears. We suggest the following explanation. Acceptor (donor) states are split in an external magnetic field. The photon absorption by the fixed DA pair leads to the population of one of the Zeeman sublevels [Fig. 4(b)]. Relaxation from the higher-lying sublevels to the lowest sublevel [pairs (v) and (vi) in Fig. 4(b)] results in the low-energy tail. The characteristic width of this tail does not change with magnetic fields because the Zeeman splittings disperse in the same manner as the polaron shifts, i.e. due to the static fluctuations of the Mn concentration. In case when the lowest Zeeman sublevel of DA pairs is excited [pair (iv) in Fig. 4(b)] a further relaxation is not possible, and the narrow line is observed at the excitation energy. With growing magnetic fields the width of this line should decrease and saturate in fields when the magnetization of magnetic ions saturates ($B > 3$ T).

It is now clear why the narrow peak is suppressed when the polarization axis of the excitation light is exact parallel to the magnetic field direction: Due to optical selection rules the excitation to the ground state [pair (iv) in Fig. 4(b)] is forbidden in this configuration. However, even a small deviation from this geometry restores the perpendicular-to-field component of the polarization vector, and the peak rises up.

III. THEORY

In order to calculate the PL spectra under selective excitation one needs to find the distribution function of the Stokes shift induced by the polaron formation in zero magnetic field. On the other hand, in case of strong magnetic fields the distribution function is determined by the Zeeman splitting dispersion. The hole (electron) spins interact with Mn ions via the p - d (s - d) exchange interaction. In case of localized carriers this interaction can be written as

$$\hat{\mathcal{H}}_{sa} = \alpha \sum_i \vec{s}_e \cdot \vec{S}_i \Psi_e^2(\vec{r}_i), \quad (2)$$

$$\hat{\mathcal{H}}_{pd} = \frac{\beta}{3} \sum_i \vec{J} \cdot \vec{S}_i \Psi_h^2(\vec{r}_i), \quad (3)$$

where \vec{s}_e and \vec{J} are the electron and hole spin operators, Ψ_e and Ψ_h are their wavefunctions, respectively. \vec{S}_i is the spin operator of the i -th Mn ion, and \vec{r}_i is a radius-vector assigning Mn location in the crystal. The exchange constants in $\text{Cd}_{1-x}\text{Mn}_x\text{Te}$ are $\alpha = 14850 \text{ meV } \text{\AA}^3$ and $\beta = 59400 \text{ meV } \text{\AA}^3$. The donor and acceptor Bohr radii are equal approximately 60 \AA and 10 \AA , respectively. This implies that the spin splitting of the Mn ion removed by the Bohr radius from the acceptor (donor) is 1.28 meV ($1.5 \mu\text{eV}$). In other words, at a temperature $T = 1.6 \text{ K}$ ($k_B T = 0.14 \text{ meV}$) the electron contribution can be neglected, and all Mn spins in the vicinity of the acceptor are aligned along the exchange field of the hole. The hole exchange energy in the ground state is $E_h = \frac{5}{4}\beta \sum_i \Psi_h^2(\vec{r}_i)$. Its mean value averaged over all Mn configurations is $\langle E_h \rangle = \frac{5}{4}\beta N_0 x$, where $N_0 = 0.015 \text{ \AA}^{-3}$ is a concentration of cations. For $x = 0.5\%$ it is equal $\langle E_h \rangle = 5.0 \text{ meV}$. The root-mean-square fluctuation $\delta E_h = \sqrt{\langle E_h^2 \rangle - \langle E_h \rangle^2}$ is equal $\delta E_h = 5.9 \text{ meV}$. And the mean value of the hole energy in the fluctuating fields of nonpolarized Mn ions $\delta E_{hf} = \frac{1}{2}\beta \sqrt{N_0 x \frac{S(S+1)}{3}} \int \Psi_h^3 d^3 r$ is equal $\delta E_{hf} \approx 5.5 \text{ meV}$. It follows from these estimations that the fluctuations of the exchange energy and its mean value are nearly the same. Therefore the Gaussian statistics and, as consequence, the mean-field approach is not applicable.

In case of low Mn concentrations it is difficult to obtain an analytical solution for the Stokes shift distribution function. Therefore, in order to calculate the PL spectra under selective excitation we use numerical computing based on the Monte-Carlo method. First, a random distribution of magnetic ions in a sphere with a radius equal to ten acceptor Bohr radii $10a_B$ is generated [see also Fig. 5(b)]¹⁷. Each Mn ion has a random spin orientation in accordance with the equilibrium distribution for a given temperature and magnetic field strength. Then, the total exchange field acting on the hole bound to the acceptor placed in the center of the sphere is calculated. After that, the eigenstates of the hole in this total exchange field and the transition probabilities on these

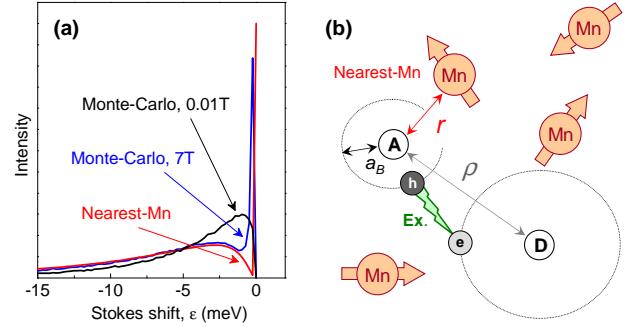


FIG. 5: (Color online) (a) Calculations of the PL spectra by the Monte-Carlo method and within the approach considering the nearest-Mn ion. Note, the nearest-Mn approach gives the same result for zero and strong magnetic fields. (b) Random distribution of acceptors (A), donors (D) and Mn ions.

states are evaluated. Polaron energies are determined for each generated Mn distribution by adding the exchange field of the hole acting on Mn ions to the external magnetic field. The Stokes shift is calculated as an energy difference between the initial and final states. Finally the distribution function of the Stokes shift is obtained after summation over 50000 realizations.

The calculated PL spectra for different magnetic fields are shown in Fig. 3(b). Not only qualitative but also quantitative agreement with experimental data [compare with Fig. 3(a)] is achieved. Note, no fitting parameters are used in the calculation.

Because of low Mn-ion count in the vicinity of the acceptor (on average there are 0.3 Mn ions inside the sphere of radius a_B) it is natural to assume that the nearest Mn ions give dominant contributions to the Stokes shifts [Fig. 5(b)]. We now consider this approach in details. In an external magnetic field the hole states are split in four sublevels characterized by the different projection J_z of the hole angular momentum on the field direction. One of them with $J_z = 3/2$ is a ground state. The contribution to the PL spectra from this state is a delta function $\delta(\varepsilon)$ (if neglecting native homogeneous broadening) as shown in Fig. 4(b) [pair (iv)]. Excitation in one of three other states is followed by relaxation to the ground state [pairs (v) and (vi) in Fig. 4(b)]. Therefore, the shift of the emission energy with respect to the excitation energy is described by the distribution function of the nearest (to the hole) Mn ion, $F_{NN}(\varepsilon)$. Then, under unpolarized excitation the distribution function $F(\varepsilon)$ of the Stokes shift ε is written as

$$F(\varepsilon) = W_{3/2} \delta(\varepsilon) + W_{1/2} F_{NN}(3\varepsilon/2\varepsilon_0) + W_{1/2} F_{NN}(3\varepsilon/4\varepsilon_0) + W_{3/2} F_{NN}(\varepsilon/2\varepsilon_0), \quad (4)$$

where $W_{3/2} = 3/4$ and $W_{1/2} = 1/4$ are the probabilities to excite the hole with $J_z = \pm 3/2$ and $J_z = \pm 1/2$, respectively. And the characteristic exchange energy is $\varepsilon_0 = \frac{5}{4}\beta \Psi_h^2(0) = 23.6 \text{ meV}$. The probability $dP_{NN}(r)$ that the nearest Mn ion is located in the spherical layer $(r, r + dr)$ [see Fig. 5(b)] is given by the probability to

find one Mn ion in this spherical layer being equal to $xN_0 4\pi r^2 dr$, and the probability that there are no Mn ions inside the sphere of radius r being equal to $P_0(r)$. Here, $P_0(r)$ is the Poisson distribution $P_n(\bar{n}) = \frac{\bar{n}^n}{n!} \exp(-\bar{n})$ with $n = 0$ and $\bar{n} = \frac{4}{3}\pi r^3 xN_0$. Then one writes

$$dP_{NN}(r) = 4\pi r^2 xN_0 \exp(-4\pi r^3 xN_0/3) dr. \quad (5)$$

Recall, the energy of the exchange interaction between the hole and Mn ion depends on a distance r as $\Psi_h^2(r)$, i.e. $\varepsilon(r) = \varepsilon_0 \exp(-2r/a_B)$ and $dr = -a_B/(2\varepsilon)d\varepsilon$. Finally, one obtains the distribution function vs energy ε as $F_{NN} = dP_{NN}/d\varepsilon$

$$F_{NN}(\varepsilon/\varepsilon_0) = \frac{3\gamma}{2\varepsilon} \left(\ln \frac{\varepsilon}{\varepsilon_0} \right)^2 \exp \left[\gamma \left(\ln \frac{\varepsilon}{\varepsilon_0} \right)^3 \right], \quad (6)$$

with $\gamma = (\pi/6)xN_0 a_B^3$.

Figure 5(a) shows that the nearest-Mn approach describes well the PL spectra in high magnetic fields. However, the agreement becomes worse for small ε in zero magnetic field, while the high-energy tail is still described quite well. The reason is that for the complex 'hole + nearest-Mn ion' the relaxation is not possible at the excitation to the ground state, and the Stokes shift is absent. This results in a δ -function peak appearing in zero as well as in high magnetic fields [first term in Eq. (4)]. In real the contribution to the Stokes shift for $\varepsilon \ll \varepsilon_0$ arises from several distant ($r \gg a_B$) Mn ions. In weak magnetic fields the spins of these distant ions are disordered, and their orientation induced by the exchange field of

the hole results in the energy lowering. In strong magnetic fields the spins are already oriented at the moment of excitation, further relaxation does not occur, which manifests itself as the appearance of the narrow peak at $\varepsilon = 0$.

IV. CONCLUSIONS

With use of the site selective spectroscopy of residual DA pairs in bulk $\text{Cd}_{1-x}\text{Mn}_x\text{Te}$ samples we are able to observe the formation of bound magnetic polarons in a very dilute ($x < 0.01$) regime. Under selective excitation the PL spectra show an asymmetric band with low-energy tail and the additional very narrow peak inflaming in external magnetic fields. This behavior cannot be described in terms of the mean-field approach, frequently applied to diluted magnetic semiconductors (DMS). Our findings suggest that the low-energy tail is formed due to the exchange interaction of the hole (bound to the acceptor) with the nearest Mn ion, and is described by the Poisson distribution. Unexpectedly, the dominant contribution to the narrow peak arises from the interaction with several Mn ions remote from the hole.

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¹⁷ Note in Ref. 4, in order to calculate BMP energies, the magnetic ions in a sphere of radius $R \sim 1.5a_B$ were considered.